

# Naval Research Laboratory

Washington, DC 20375-5000



2

NRL Memorandum Report 6848

AD-A239 276



## Dilatometry on Thermoset Resins

ARTHUR W. SNOW AND J. PAUL ARMISTEAD

*Materials Chemistry Branch  
Chemistry Division*

July 29, 1991

DTIC  
ELECTE  
AUG 8 1991  
S B D

91-07078



Approved for public release; distribution unlimited.

91 8 06 062

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 1991 July 29	3. REPORT TYPE AND DATES COVERED		
4. TITLE AND SUBTITLE  Dilatometry on Thermoset Resins		5. FUNDING NUMBERS		
6. AUTHOR(S)  Arthur W. Snow and J. Paul Armistead				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Naval Research Laboratory Washington, DC 20375-5000		8. PERFORMING ORGANIZATION REPORT NUMBER  NRL Memorandum Report 6848		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Office of Naval Research Arlington, VA		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.		12b. DISTRIBUTION CODE  15		
13. ABSTRACT (Maximum 200 words)  A simple capillary and bulb mercury dilatometer designed for making specific volume measurements on thermoset resin systems during the curing reaction and as a function of temperature is described. The design, calibration, operation, data treatment and error analysis are presented in detail with data on the bisphenol A dicyanate resin system used as an example. Particular attention is directed at experimental difficulties such as monomer/prepolymer degassing, filling the dilatometer under vacuum, adhesive distortion of the curing resin on the dilatometer bulb and the dilatometer bulb to capillary connection problem. <i>(to pg 1)</i>				
14. SUBJECT TERMS Dilatometry Thermoset shrinkage Thermal expansion		Specific volume Cyanate resin		15. NUMBER OF PAGES 25
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	16. PRICE CODE
20. LIMITATION OF ABSTRACT UNLIMITED				

## CONTENTS

I.	INTRODUCTION .....	1
II.	DILATOMETER DESIGN .....	2
	Features and Obstacles .....	2
	a) Parts Description .....	2
	b) Adhesion of Thermoset to Dilatometer Bulb ..	4
	c) Bulb to Capillary Connection .....	5
	d) Degassing .....	6
	e) Dilatometer Confining Fluid .....	6
	f) Filling Under Vacuum .....	6
	Quantitative Aspects .....	6
	a) Basic Equation .....	6
	b) Selection of Bulb Size and Mercury:Polymer Volume Ratio .....	8
III.	CALIBRATION .....	9
IV.	OPERATION .....	9
	Cleaning.....	9
	Bulb Surface Treatment .....	11
	Thermoset Degassing .....	11
	Dilatometer Assembly and Filling .....	12
	Data Collection .....	13
	a) Monomer Thermal Expansion .....	13
	b) Thermoset Cure .....	13
	c) Cured Thermoset Thermal Expansion .....	14
V.	DATA TREATMENT .....	14
VI.	ACCURACY AND ERRORS .....	16
	Propagation of Errors .....	19
	Repetitive Measurements .....	19
VII.	ACKNOWLEDGEMENT .....	20
VIII.	REFERENCES .....	21

# DILATOMETRY ON THERMOSET RESINS

## INTRODUCTION

In a general sense, dilatometry involves dimensional measurements on matter. Volume dilatometry is the measurement of volume for a specific mass of matter. The state of matter may be solid, liquid or gas, and the influences of chemical structure, morphology, chemical reaction, temperature and pressure are studied. The design and operation of a dilatometer are dependent on the type of matter and physical variables being studied. In this work, we are primarily concerned with volume changes accompanying the cure reaction and thermal expansion of thermoset polymers. This report is a detailed account of customizing the design of a dilatometer to make such measurements. Thermoset polymers present somewhat unique challenges in that the material starts as a viscous liquid and transforms into a rigid solid with excellent adhesive properties. It is this characteristic that makes these materials useful as composite matrix resins.

The need for volume change information accompanying thermoset cure and thermal expansion/contraction connects fundamental chemistry with practical applications and impacts on processing, mechanical properties, interfacial adhesion, internal stress and fatigue of these materials. Processing, especially with molds, places a threshold on the amount of cure and thermal shrinkage which vary significantly with cure temperature. Mechanical properties depend on the amount of free volume which may be locked in via chemical structure and thermal quenching. Interfacial adhesion may correlate with a thermal expansion mismatch and a postvitrification volume change during cure. Internal stress may also result from postvitrification volume change as well as free volume shrinkage from aging of a glassy state. Likewise, fatigue may correlate with free volume shrinkage from stress and aging of a glassy state.

Literature reviews on dilatometry may be traced back to an 1894 text by Ostwald [1], but it is not a very popular topic for modern physical chemistry books. A 1949 review by Bekkedahl [2] is the most cited reference for experimental detail. A 1973 reference by Wilson and Simha [3] also presents very useful experimental information for simple dilatometers. Specific to polymers, reviews in the Encyclopedia of Polymer Science and Technology [4] and Encyclopedia of Polymer Science and Engineering [5] provide good general coverage of dilatometry on polymer systems and, in the former case, of dilatometer design. However, little is said about details of problems unique to

thermoset polymers. References 6-9 report dilatometric measurements on thermoset systems most of which are epoxy. References 4 and 10 contain information relevant to thermoset dilatometry. Comments regarding these references will be made where pertinent individual details are being discussed.

The objective of this report is to describe a simple (i.e. constructible from commercially available glassware with routine glassblowing skills) and versatile dilatometer designed specifically for measurements on thermoset polymers. These measurements include specific volumes of monomers and cured polymers, the volume coefficient of thermal expansions and the specific volume change of the cure reaction. Experimental obstacles such as monomer/prepolymer degassing, filling the dilatometer under vacuum, adhesion distortion by the cured resin on the dilatometer, and the dilatometer bulb to capillary seal will be discussed along with a detailed operational procedure and data workup.

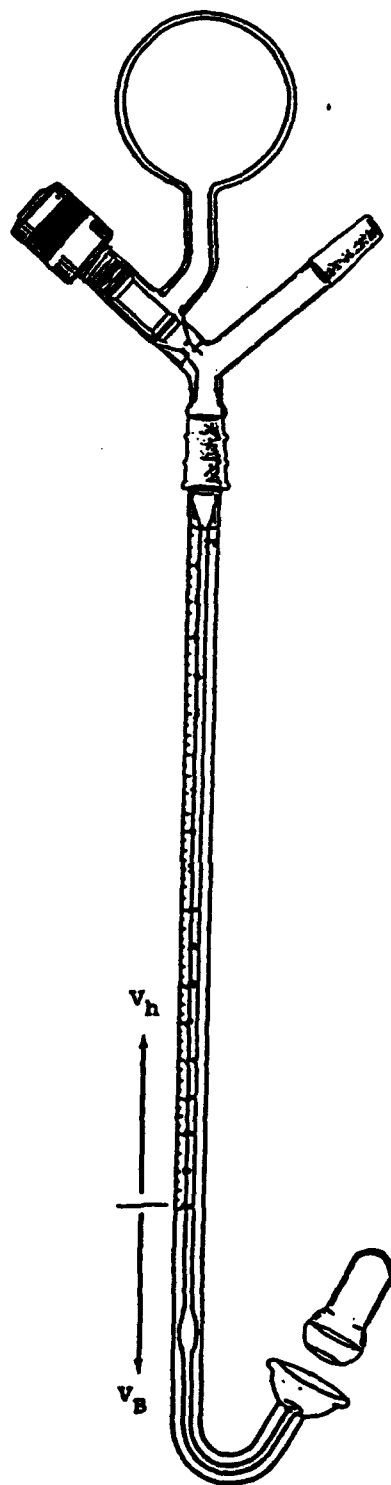
## DILATOMETER DESIGN

### Features and Obstacles.

a) Parts Description. A drawing of the dilatometer used in this work is presented in figure 1. It consists of three main parts: a detachable bulb, a graduated precision bore capillary and a filling apparatus. The bulb is constructed from a 18/9 standard ball joint. The joint is sealed with a rounded end as in the drawing with a mouth to tip length of approximately 32 mm. The sealing should be done so that there is no enlargement in tube diameter or the cured thermoset will not eject through the mouth of the ball joint. This bulb is approximately 2 ml in volume and easily accommodates 1 gram of thermoset.

The precision bore capillary (diameter of 1.02 to 1.07 mm and graduated length of 40 cm) with the bend and socket joint at the bottom is obtained commercially (Ace Glass, Vineland, NJ; Volumetric Dilatometer, Catalog Number 6283). With the services of a glassblower the 12/5 socket joint is replaced with an 18/7 standard socket joint (preferably from the same vendor from whom the bulb ball joint was obtained) and a 10/30 standard taper inner joint is attached to the upper end for connection to the filling apparatus. The volume of the capillary end to socket joint connection should be minimized to preserve the accuracy of a good mercury to polymer volume ratio which is two to one in the present case.

The filling apparatus is constructed from a polytetrafluoroethylene valve (Kontes, Vineland, NJ; PTFE Valve with bent sidearms, 4 mm bore, Catalog Number 826620-0004), a 35 ml bulb, a 10/30 standard taper outer joint and a vacuum manifold connecting joint (in this case a standard taper 12/30 inner joint). The PTFE valve allows for vacuum storage of the mercury in the bulb and for control of the mercury transfer rate when



**Fig. 1.** Dilatometer design used in this study. The zero line indicated demarcates the dilatometer bulb volume,  $V_B$ , from the capillary volume,  $V_h$ .

filling the dilatometer. The bends in the sidearms of the PTFE valve are well-suited for straight-on connections to the bulb and capillary connecting joint. The manifold connecting joint may connect vertically beneath a vacuum manifold or to flexible vacuum tubing. For the vertical manifold connection, the angle of this joint is determined by an orientation which will permit dropwise quantities of mercury to pass through the valve and slide down the capillary to fill the dilatometer bulb with relative ease. This orientation is closely parallel to the top sidearm of the valve and can be finely adjusted with a torch until the best compromise angle is found. The capillary connecting joint may be rotated to orient the dilatometer bulb for the mercury filling operations. This joint should also be reinforced with a plastic clamp or springs/hooks during these operations.

b) Adhesion of Thermoset to Dilatometer Bulb. Since most thermosets have very good adhesive properties, two serious dilatometry problems arise as a consequence of the resin to bulb adhesion produced during the curing reaction. Stress, both internally on the thermoset and externally on the dilatometer bulb, is generated as the specific volume of the thermoset changes relative to the volume of the bulb. This stress distorts the volume measurement by perturbing the thermoset from its equilibrium state, generating microvoids and deforming the bulb. In many cases when the bulb wall is not thick enough to withstand the stress, the result is catastrophic. The second problem is ejection of the cured thermoset after the measurement and preservation of the calibrated bulb. Damage-free detachment of the resin from the bulb is frequently impossible.

In the literature two techniques are used to address this resin adhesion problem. One method is to encapsulate the monomer or prepolymer in a flexible thin film bag made of poly(vinyl fluoride) [6], polycaprolactam [6] or emulsoid rubber [9] which is subsequently placed in the dilatometer bulb. The contribution of the bag to the volume measurement must of course be corrected for if not negligible, and the bag must be stable and inert under conditions of the measurement. The other method involves coating the interior of the bulb with a "parting agent" composed of silicone vacuum grease. This was reported to be unsatisfactory [7]. The bag method has the convenience of a facile removal of the resin after the measurement but the complication of procurement, filling, sealing, invoking a correction factor and stability limitations (chiefly temperature).

The approach in this work was to identify a pyrex glass surface treatment which prevents adhesion of curing thermoset resins. This has the advantage of eliminating a correction factor in the dilatometer measurement. The testing involved curing a one gram quantity of Epon 828 (Shell Chemical Co.) in a 10 x 75 mm surface treated Pyrex tube and determining that the cured resin plug could be removed by simple inversion and tapping. The surface treatment products tested included (1)

MS122 (PTFE solids spray-on mold release agent, Miller-Stephenson Chemical Co., Danbury, CT), (2) MS136 (fluorocarbon spray-on mold release agent, Miller-Stephenson Chemical Co., Danbury, CT), (3) Frekote 700 (proprietary resin release spray-on release agent, Frekote, Seabrook, NH), (4) 3M Silicone Lubricant (Siloxane mold release spray, 3M Company, St. Paul, MN), (5) perfluoroparaffin wax (Fisher Chemical Co., Silver Spring, MD), (6) Glassclad 18 (monomeric octadecylsilanol siliconizing reagent, Petrarch Systems, Bristol, PA) and (7) Glassclad 6C (chlorine terminated polydimethylsiloxane telomer siliconizing reagent, Petrarch Systems, Bristol, PA). Only the Glassclad 6C passed the testing. Failures ranged from catastrophic implosion to resin cracking to non-release. The Glassclad 6C had the further advantage that it could be cycled many times without loosing its release properties. However, a treated surface should not be contacted with concentrated nitric acid which is used to clean mercury residues from the capillary. Nitric acid contact causes the surface to become opalescent and lose its release properties. The precision bore capillary component of the dilatometer should not be surface treated. The surface treatment may be removed by brief contact with 30% hydrofluoric acid, but such treatment makes recalibration necessary.

c) Bulb to Capillary Connection. Since the thermoset cure results in a liquid being transformed to a non-melting, insoluble solid, the dilatometer used to monitor the cure reaction must be designed for removal of the cured resin. The alternatives are a burn-away oxidation or an acid digestion both of which can be very messy and time consuming as well as detrimental to a release surface treatment. For resin removal, the mechanical requirement is a wide mouth connection on the dilatometer bulb. An operational requirement is that the connection be vacuum tight for the degassing and filling procedures and stable at measurement temperatures. Further, if variable temperature measurements are being made, the connection should not contribute to the volume measurement.

To make this connection, an O-ring [6] and standard taper joints [3,10] have been used. The O-ring has the appeal of being a greaseless vacuum tight mechanical seal. Restrictions are: (1) the O-ring must totally compress within its groove such that the rigid surfaces of the connection are intimately in contact and remain so at elevated temperatures in order not to add to the volume of the bulb, and (2) the O-ring be stable and not out gas at resin cure temperatures which may be as high as 250°C. The standard taper joint if made of ground glass requires grease for a vacuum tight seal. While the vacuum grease film between the joint surfaces is easily thin enough not to perturb the bulb volume, its spreading when the joint surfaces are brought into initial contact can result in a milligram or submilligram quantity migrating to the inner edge of the joint contact area. This can translate into a  $10^{-3}$  ml/g specific volume error.

The initial approach in this work is to employ a standard

ball and socket joint for this connection. The vacuum grease problem still exists (vide infra), but the ball and socket joint dimensions are such that less volume is added to the bulb compared with the taper joint. Current efforts to circumvent the vacuum grease problem involve trial of an O-ring ball joint and use of greaseless clear-seal joints. Clear-seal joints (Wheaton, Millville, NJ) are only available in standard taper form at minimum size of 14/20. Trial of a cut-down clear-seal joint of this size is in progress.

d) Degassing. Residual solvent, dissolved air, occluded air and volatile byproducts of initiators are very detrimental to the specific volume measurement especially at elevated cure reaction temperatures. For example, 1 microgram of volatile impurity at a 200°C cure temperature can produce a 1 mm diameter bubble with a volume of 0.0005 ml. A very brief reduced-pressure stirred degassing of the monomer or resin prepolymer at the cure temperature followed by transfer to the dilatometer and a second very brief degassing within the dilatometer before filling with the confining fluid is good insurance against traces of volatiles disrupting the volume measurement. The severity of the degassing conditions is dependent on the vigor of the cure reaction and the importance of initial cure reaction data points.

e) Dilatometer Confining Fluid. Mercury offers many advantages as the choice for the confining liquid. These include: (1) total insolubility in and nonreactivity with the resin, (2) stability, nonvolatility and very accurately known expansion over the temperature range of interest and (3) a large density which enhances precision of the dilatometer calibration. This large density has the disadvantage that the dilatometer bulb must be inverted during filling and operation to prevent the molten monomer or prepolymer from plugging the capillary. Silicone oil has also been used as a confining fluid [9].

f) Filling under Vacuum. For simple dilatometers using mercury as the confining fluid, the filling apparatus consists of a three way stopcock fixed to the top of the capillary which alternately connects the dilatometer to a vacuum source and a mercury reservoir [2,3]. More complicated dilatometers fill from beneath the capillary which makes for better control of the filling operation but complicates the weighing and heating operations. The PTFE valve arrangement in figure 1 has the advantages of fine control of the mercury dispensing rate, has no grease to contact with the mercury and allows for facile return of the mercury from the capillary to the reservoir.

#### Quantitative Aspects.

a) Basic Equation. For calculation purposes, the volume of the dilatometer is divided into contributions from two components; that of the capillary,  $V_h$ , and that of the bulb,  $V_b$ . The demarkation between the two is the zero line on the capillary graduation as indicated in figure 1, and the capillary volume is

determined by the height of the mercury in the capillary. The volume of the polymer in the bulb,  $V_p$ , is then the difference between the measured sum of the capillary and bulb volumes and the volume occupied by the mercury,  $V_{Hg}$ .

$$V_p = (V_h + V_B) - V_{Hg}$$

Keeping the representative quantities in the same order, this equation achieves a more useful form expressed as a polymer specific volume,  $V_{sp}$ , with the capillary volume expressed as a cylinder and with thermal expansion correction terms for Pyrex glass and mercury added in a manner similar to that done in reference 2.

$$V_{sp} = (1/W_p) [(\pi(d/2)^2 h + V_B)(1 + \beta_{py}(T-25)) - W_{Hg}(V_{sp,Hg}(1 + \beta_{Hg}T))]$$

Where:

- $W_p$  - mass of resin in the dilatometer (grams)
- $d$  - diameter of dilatometer capillary (cm)
- $h$  - height of mercury in dilatometer capillary (cm)
- $V_B$  - calibrated volume of dilatometer bulb (cm<sup>3</sup>)
- $\beta_{py}$  - Pyrex glass volume coefficient of thermal expansion at 25°C (0.000010 °C<sup>-1</sup>) [2]
- $T$  - temperature of dilatometer bulb (°C)
- $W_{Hg}$  - mass of mercury in the dilatometer (grams)
- $V_{sp,Hg}$  - mercury specific volume at 0°C (0.073554 cm<sup>3</sup>/gram) [2]
- $\beta_{Hg}$  - mercury volume coefficient of thermal expansion at 0°C (0.000182 °C<sup>-1</sup>) [11]

The circular cross-section of the capillary is determined by the dilatometer calibration (see following section), and the quantity  $\pi(d/2)^2$  is replaced by the capillary calibration constant,  $c$ . Also, if the capillary emerges from the temperature control bath, a stem correction similar to that used for thermometers for the differential thermal expansion of the Pyrex glass and mercury should be made. These expressions are as follows:

$$c = \pi(d/2)^2$$

$$\text{stem correction} = c(\Delta h)(\beta_{Hg} - \beta_{py})(\Delta T)$$

where  $\Delta h$  is the mercury filled capillary length above the temperature bath and  $\Delta T$  is the temperature difference between the bath and the midpoint of  $\Delta h$  (close to room temperature). Incorporating these expressions into the specific volume equation gives the following working equation for the dilatometer.

$$V_{sp} = (1/W_p) [(ch + V_B)(1 + \beta_{py}(T-25)) + c(\Delta h)(\beta_{Hg} - \beta_{py})(\Delta T) - W_{Hg}(V_{sp,Hg}(1 + \beta_{Hg}T))] \quad (1)$$

The calibration establishes the dilatometer values of  $c$  and  $V_B$ , and the values of  $W_p$ ,  $W_{Hg}$ ,  $h$  and  $T$  are taken as data during the experiment with the resin.

b) Selection of Bulb Size, Capillary Size and Mercury:Polymer Volume Ratio. In designing a dilatometer, the magnitude of the volume change is a key consideration for the selection of precision bore capillary and bulb sizes. For temperature dependent measurements, the volume ratio of confining fluid to polymer has a strong affect on the precision. The thermal expansion of the fluid may also need to be considered. As a guide for such design considerations, the following equation has been found to be useful.

$$\frac{\Delta V_p}{V_p} = \frac{\pi(d/2)^2 \Delta h}{\phi V} - \beta_{Hg} \Delta T \quad (2)$$

Where:

- $\Delta V_p/V_p$  - fractional change in resin volume
- $d$  - diameter of dilatometer capillary (cm)
- $\Delta h$  - length of capillary to accommodate volume change (cm)
- $\phi$  - volume fraction of resin in mercury-polymer combination
- $V$  - volume of dilatometer (cm<sup>3</sup>)
- $\beta_{Hg}$  - mercury volume coefficient of thermal expansion (0.000182 °C<sup>-1</sup>)
- $\Delta T$  - temperature range for dilatometer measurement (°C)

Equation 2 may be used to calculate the magnitude of volume change a dilatometer with particular design characteristics can accommodate. The first term on the right of the equal sign contains the dilatometer's critical dimensions and the effect of the confining fluid to resin volume ratio. The second term

accounts for the thermal expansion of the confining fluid over the temperature range of the measurement. As an example consider a dilatometer with a 1 mm diameter capillary, a 20 cm effective length, 3 ml volume, a 2:1 mercury to resin volume ratio ( $\phi=0.33$ ) and a thermoset that cures at 200°C ( $\Delta T=175^\circ\text{C}$ ). Then,  $\Delta V_p/V_p = 0.16 - 0.03 = 0.13$  or about a 13% prepolymer volume change. If the polymerization process causes shrinkage, then, after reaching cure temperature equilibrium,  $\Delta V_p$  becomes negative, and the limit of shrinkage measurable is 19% since this effect is opposite to the thermal expansion of the mercury.

## CALIBRATION

The dilatometer is calibrated for two parameters, the capillary constant,  $c$ , and the dilatometer bulb volume,  $V_b$ . The capillary constant is the volume per unit height (or circular cross section assuming a cylindrical shape) of the capillary. The dilatometer bulb includes the capillary volume up to the point where the graduated markings begin. To obtain these calibration parameters the dilatometer is filled with mercury (see following section) to various heights in the capillary, and the mass and capillary height of the mercury are recorded. The mass measurements of mercury are converted to volumes via equation 3, and a plot of volume vs capillary height is constructed (figure 2).

$$V = W_{\text{Hg}} (V_{\text{sp, Hg}} (1 + \beta_{\text{Hg}} T)) \quad (3)$$

The slope and intercept of the calibration plot yield the respective values for  $c$  and  $V_b$ . The uniformity of the capillary along its length is reflected in the linearity of the plot. In the example of figure 2, the respective values of  $c$ ,  $V_b$  and the linear correlation coefficient are 0.0086696 ml/cm, 2.5293 and 0.999997. A capillary diameter of 0.1051 cm may be calculated from the value of  $c$  and is within the precision range (1.02-1.07 mm) quoted by the manufacturer.

## OPERATION

### Cleaning.

A good cleaning is recommended if the dilatometer is newly constructed or mercury residues are observed adhering to the capillary. For the capillary and filling apparatus the following sequence has been found to work well: concentrated nitric acid to remove mercury residues (with hot air heating if necessary); water rinse, acetone flush and methylene chloride to remove vacuum grease; 1:1 mixture of concentrated nitric and sulfuric acids for trace organic films; distilled water rinse and vacuum drying. If the bulb has been surface treated with siliconizing agent, it should not be contacted with nitric acid but cleans easily with acetone and water rinses.

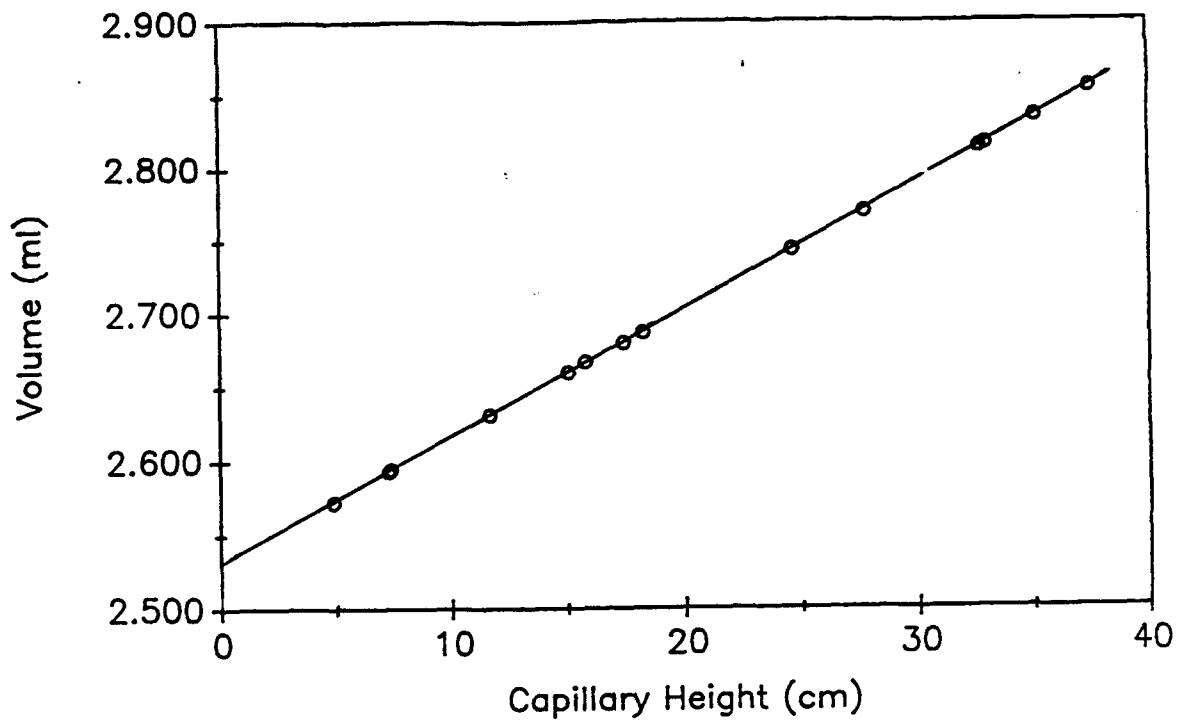


Fig. 2. Dilatometer calibration plot to obtain capillary constant and dilatometer bulb volume.

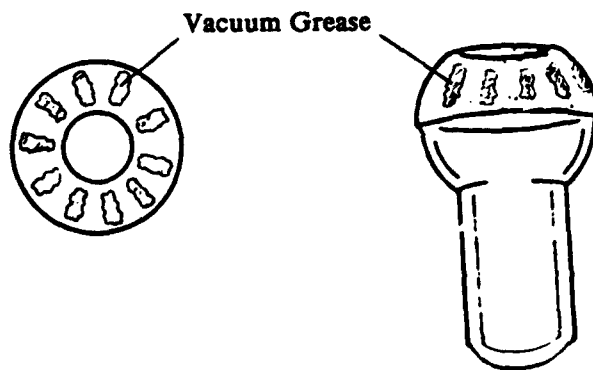


Fig. 3. Vacuum grease application pattern on dilatometer bulb ball joint.

### Bulb Surface Treatment.

This treatment involves contacting the inside surface of the dilatometer bulb with a series of solutions. For convenience, the bulb is positioned upright standing in the neck of a vial supported by the larger diameter of the ball joint. The solutions are transferred to and from the bulb with a clean medicine dropper to avoid solution contact with the surface of the ball joint. The bulb is first filled with a 50% hydrofluoric acid solution (J.T. Baker Chemical Co., Phillipsburg, NJ) for 15 seconds, emptied and rinsed with distilled water. It is then filled with a 3% NaOH solution for 60 seconds, emptied, rinsed thoroughly with distilled water and dried at 110°C for 60 minutes. After cooling, the bulb is filled with a 5% solution of Glassclad 6C (Petrarch Systems, Bristol, PA) in methylene chloride, emptied and dried at 110°C for at least 20 minutes before use.

The release properties from this treatment have survived as many as 5 dilatometer measurements of cyanate resin cure at temperatures approaching 225°C. The treatment is also effective for multiple epoxy cures at 125°C. When the release appears to be deteriorating, the treatment can be renewed by starting at the NaOH solution treatment in the above paragraph. The calibration is not perturbed by this treatment renewal.

The treatment may be removed by contact with nitric acid followed by lifting off of the clouded film by filling with the 50% hydrofluoric acid. Retreatment can then be done, but recalibration is necessary.

### Thermoset Degassing.

The degassing conditions depend on the volatility of the thermoset monomer or prepolymer and the curing agent or catalyst. Ideally, the initial cure temperature, usually selected for at least a two hour reaction time, is used for the degassing, and the vacuum is adjusted to avoid resin component loss. The degassing time is also minimized to minimize thermoset cure conversion.

It had been found advantageous to do the degassing in two stages. In the first stage one to two grams of monomer or prepolymer in a small round bottom flask is placed in a preheated bath. The resin is magnetically stirred, and the pressure is gradually reduced such that distillation or sublimation does not occur. This is done over a 10 to 15 minute period. Since a curing additive has not been added, conversion is not much of a concern. The curing agent or catalyst should be separately degassed if practicable. In the second stage, the appropriate quantity of curing agent or catalyst is added to the molten resin, stirred and the pressure quickly reduced. Once the previous vacuum is obtained, the stirring is continued for one to two minutes. The resin is then rapidly transferred via preheated

medicine dropper if necessary to the preweighed dilatometer bulb. It is also possible to degas again after the bulb is connected and the dilatometer evacuated before filling. This last degassing may be helpful if resin crystallization is a problem.

#### Dilatometer Assembly and Filling.

After the resin has been transferred to the bulb and weighed, dilatometer assembly and mercury filling should be done without delay to avoid diffusion of air into the resin. If the resin is a room-temperature flowing liquid, the dilatometer parts (vacuum greased bulb, dilatometer capillary and clamp) have to be weighed separately for a tare weight before filling with mercury.

Vacuum grease (High Vacuum Silicone Grease, Cat. No. 970V, Dow Corning, Midland Michigan) is applied carefully and sparingly as illustrated in the drawing of figure 3. The idea is to apply the minimum quantity of grease positioning it in lines radiating out from 2 or 3 mm just short of the inside edge of the ball joint so that, when the ball is seated into the socket of the capillary, the grease will spread smoothly displacing air and connecting with adjacent lines. It is very important to avoid excess grease migrating beyond the inside edge of the ball joint and contributing to the specific volume measurement. If the resin is a room-temperature liquid, the bulb must of course remain upright at this time to prevent the resin from contacting with the dilatometer capillary. A spring-loaded pinch clamp with a screw-locking device is placed on the joint with the screw-lock tightened with maximum finger pressure. The tight locking of this clamp has solved the problem of mercury leakage through the joint during measurements at elevated temperatures.

If the resin is a solid, the tare weight before the mercury addition is now determined. An electronic balance with a draft shield and vertical access to the weighing chamber (Metler AE100) is convenient. A dilatometer holder for the balance pan can easily be made by notching an inverted pair of nested polystyrene coffee cups.

The filling apparatus (with mercury stored under vacuum in the reservoir) is connected to the dilatometer capillary and to the vacuum manifold. This is a flexible hose connection if further degassing is to be done or the resin is a liquid. With the bulb upright, a final degassing may be done at this time using gentle electric air gun warming. The resin is then solidified with liquid nitrogen cooling if necessary while pulling a vacuum of  $5 \times 10^{-3}$  mm or better for at least 5 minutes. The manifold connecting joint of the filling apparatus is connected vertically beneath a vacuum manifold or, the dilatometer is simply oriented into this position if a flexible tubing connection has already been made. The capillary to filling apparatus joint should be rotated so that the dilatometer bulb is below the level of the capillary. If there is a liquid resin the bulb, the mercury filling must be started before the

resin has had time to warm and flow to the joint connection. The valve to the mercury reservoir is very gradually opened until a very slow trickle of mercury flows. This can be initiated by a gentle tapping on the valve as the Teflon to glass contact becomes weak. The dilatometer should be filled to the first 5 to 10 cm of the capillary height. After closing the mercury valve a bead of mercury may be setting in the entrance of the capillary. This may be pushed down to join the mercury in the bottom of the capillary by very slowly bleeding air into the manifold. The dilatometer is disconnected from the filling apparatus and very slowly lowered holding a beaker underneath to catch a bead of mercury that may be resting on the taper joint lip. The vacuum grease is thoroughly cleaned off the capillary taper joint with a methylene chloride wetted tissue. Any very small beads of mercury spotted inside the taper joint are coaxed out with a wire. The dilatometer is then weighed for the mercury mass determination.

A small amount of settling (1 to 2 mm drop in the mercury level) occasionally occurs an hour or so after filling. A settling time of 2 hours or longer after filling is recommended.

#### Data Collection.

Two types of experiments are conducted: specific volume measurements as a function of cure reaction time and thermal expansion measurements on the monomer/prepolymer and cured thermoset. It is possible to do both on the same sample if the cure reaction is negligibly slow over a sufficient temperature range for enough expansion measurements to be made. This is the case for the uncatalyzed cure of bisphenol A dicyanate (AROCY B-10 monomer, contributed by D.A. Shimp, Rhone-Poulenc, Louisville, KY), and it will be used as an example.

a) Monomer Thermal Expansion. The dilatometer is clamped vertically above a temperature controlled bath with the bulb immersed about 1 inch and the immersion depth on the capillary recorded for the stem correction. A thermometer is also positioned with its bulb immediately adjacent to the dilatometer bulb. Equilibration occurs in 5 to 10 minutes and the temperature and height of mercury in the dilatometer are recorded. The bath temperature is stepped up 5 to 10°C, and temperature-dilatometer data recorded after equilibration. As the melting point of this monomer (82°C) is approached, additional equilibration time is necessary for the fusion process. After the upper end of the temperature range is reached, measurements are made in the decreasing temperature direction. In this example, the monomer may be supercooled to room temperature extending the temperature range for monomer melt thermal expansion measurements.

b) Thermoset Cure. The temperature controlled bath is preheated to the cure temperature (200°C), and the dilatometer and thermometer are immersed and positioned as described above. The

cure time and mercury column height are recorded at rapid intervals (1 minute) at first then less frequently as the specific volume change becomes slower. During the cure, mercury can be observed to fill much of the space between the bulb wall and resin plug as the gel point is passed and the resin continues to contract. Eventually, the specific volume becomes constant. Postcure measurements at higher temperatures may be continued.

c)Cured Thermoset Thermal Expansion. These measurements are made after cooling in the direction of increasing then decreasing temperature as was done above for the monomer.

#### Dilatometer Emptying and Disassembly.

To remove the mercury the dilatometer is reconnected to the filling apparatus which is connected to a vacuum via a flexible tube. The dilatometer is evacuated, and the mercury induced to flow back into the reservoir by manually tilting the manometer. Careful transfer of the mercury can leave the capillary free of mercury beads. The clamp is removed, and the bulb is detached. After cleaning the exterior and joint surface, the resin plug is ejected usually by gentle tapping along with some residual mercury beads.

#### DATA TREATMENT

All data reduction involves conversion of the mercury capillary height readings to specific volumes for which Equation 1 is used. This is programmable into a pocket calculator or minicomputer. The specific volume is then plotted as a function of temperature or of cure time. This is illustrated for the cyanate resin in figures 4 and 5.

The specific volume vs temperature plot is particularly useful as the volume coefficients of thermal expansion for the crystalline and molten monomer and cured polymer may be obtained from the slopes of the plot and the specific volumes of monomer fusion and of resin cure may be obtained from the vertical displacements. For the cyanate resin example these values are calculated as follows.

Volume coefficient of thermal expansion definition

$$\beta = \frac{1}{V_0} \frac{dV}{dT}$$

$V_0$  - specific volume at 0°C

Crystalline Monomer

$$\beta_{M,C} = (1/.813)(7.72 \times 10^{-5}) = 9.49 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$$

Molten Monomer

$$\beta_{M,M} = (1/.843)(5.80 \times 10^{-4}) = 6.89 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$$

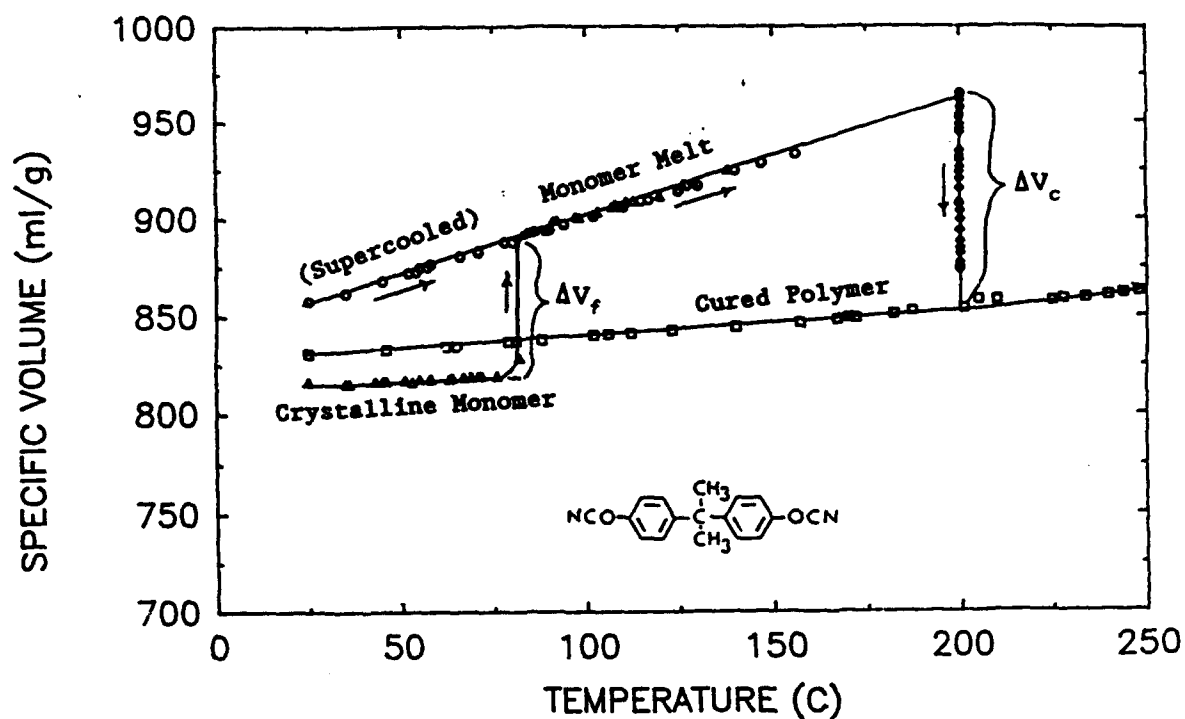


Fig. 4. Bisphenol A dicyanate specific volume - temperature data.

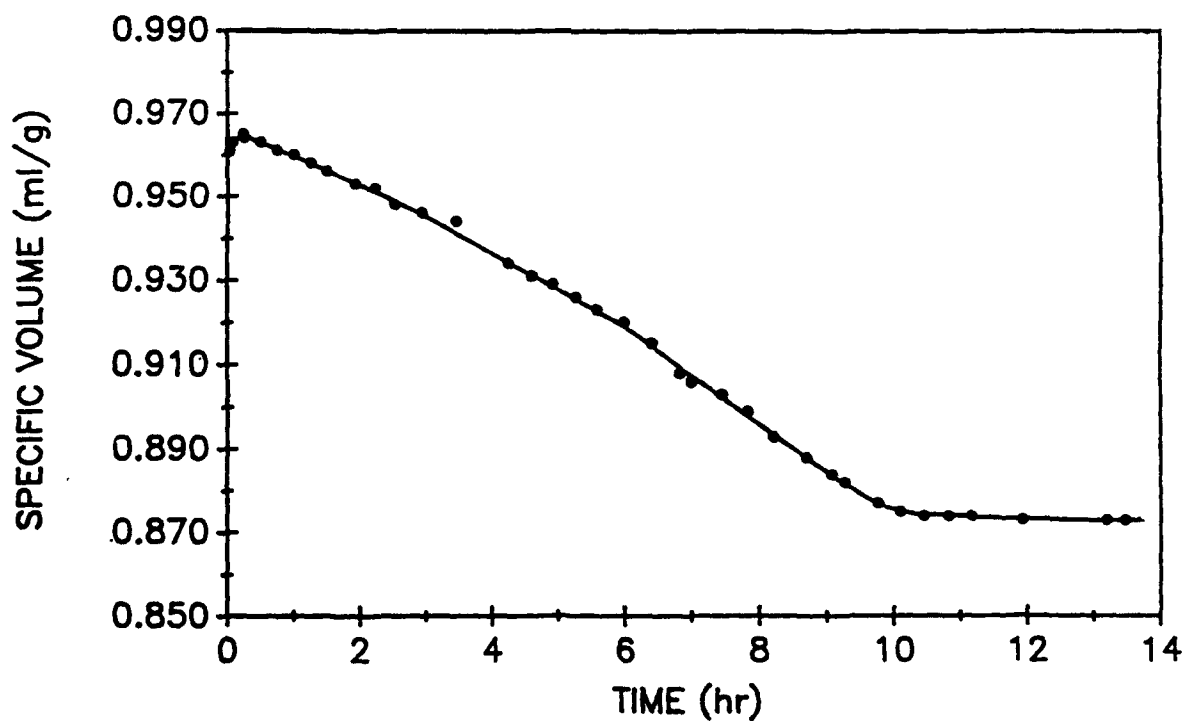


Fig. 5. Bisphenol A dicyanate specific volume - cure time data.

#### Cured Thermoset

$$S_p = (1/.828)(1.30 \times 10^{-4}) = 1.57 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$$

#### Specific Volume of Fusion

$$\Delta V_f^T = 0.071^{82^\circ\text{C}} \text{ ml/g}$$

#### Specific Volume of Cure

$$\Delta V_c^T = 0.105^{200^\circ\text{C}} \text{ ml/g}$$

Two features of figure 4 are noteworthy. The data points taken for the thermoset cure do not show shrinkage extended to the thermal expansion line of the cured polymer. Current thinking is that this gap may be due to the space that develops between the dilatometer bulb wall and cured resin plug may be too small for the mercury to completely penetrate until additional thermal shrinkage occurs after cooling to room temperature. The second feature is that estimates of the specific volume of cure for other cure temperatures may be made from the plot. This involves reading the volume difference at other temperatures between the monomer melt and cured polymer thermal expansion lines and assumes little specific volume dependence at high degrees of conversion.

In figure 5 the specific volume during cure at 200°C continually decreases for 10 hours then levels off at a constant value. This leveling off value should be considered with caution. It does not necessarily mean that cure conversion has stopped nor does it appear to be free of a dilatometer bulb wall effect described in the paragraph above and illustrated in figure 4. A more meaningful plot is one of specific volume against degree of conversion. This data is obtained from partially cured samples analyzed for cure conversion. Figure 6 displays such a plot for the bisphenol A dicyanate resin with measurements made at 20 and 200°C. It is noteworthy that the 20°C measurement indicates an apparent expansion occurs beyond 60% conversion while the 200°C measurement does not. Current thinking is that this is an effect of an advancing glass transition temperature with degree of conversion. Data for this effect is illustrated in figure 7. Thermal expansion has a greater temperature dependence above than below the glass transition. Advancement of cure may cause a small shrinkage, but the increase in glass transition temperature results less "rubbery" shrinkage on cooling and a crossover to an apparent expansion if the volume measurement is made at room temperature. This effect is illustrated in figure 8.

#### ACCURACY AND ERRORS

To obtain an assessment of the accuracy of the measurements with the dilatometer described in this report, it is possible to do propagation of errors calculation and check it with a series of repetitive measurements.

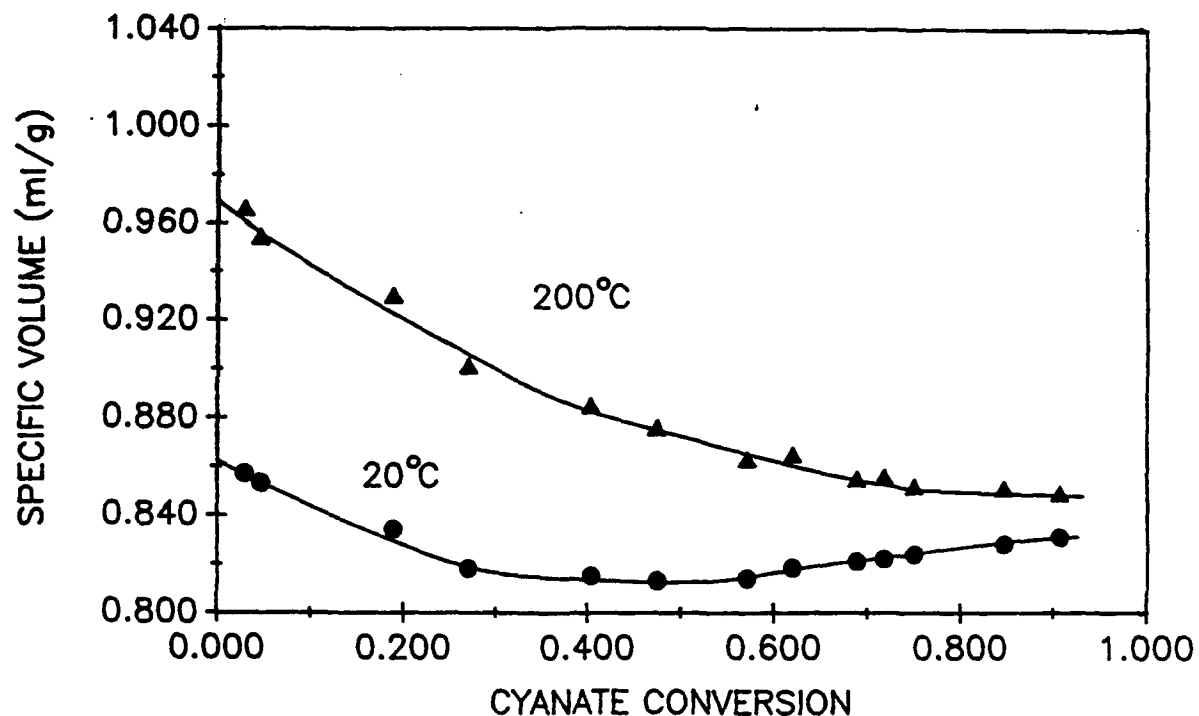


Fig. 6. Bisphenol A dicyanate specific volume measurements at cure (200°C) and room (20°C) temperatures as a function of cyanate conversion.

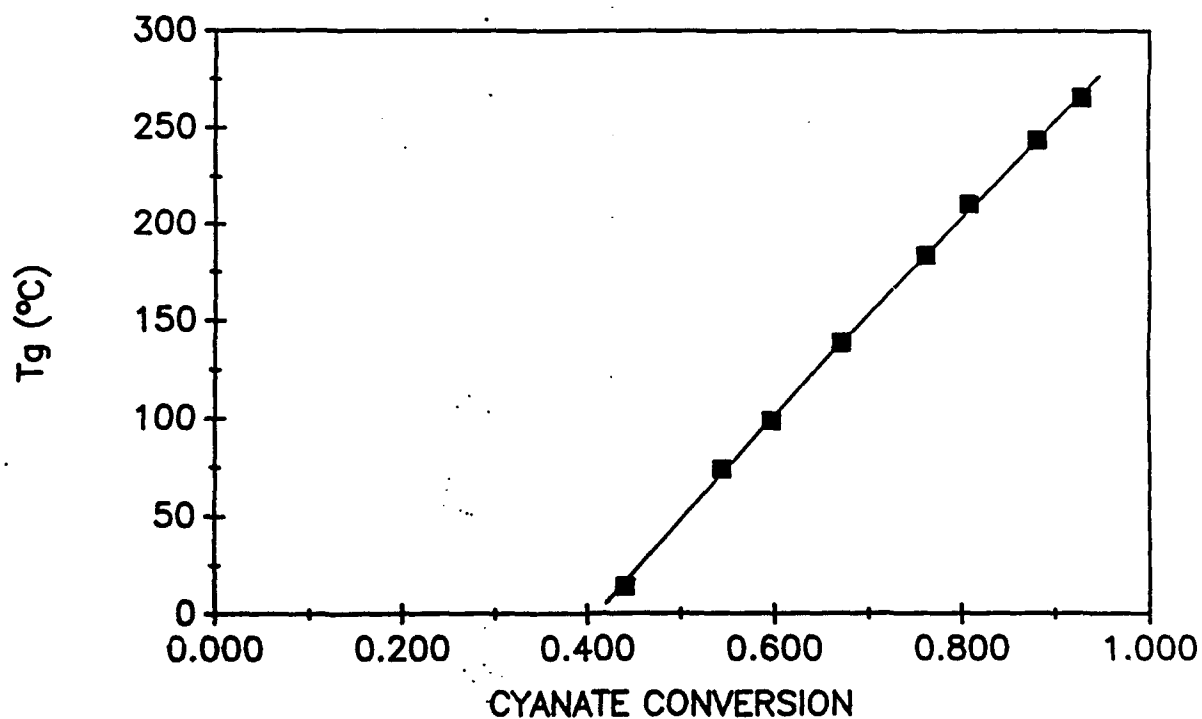
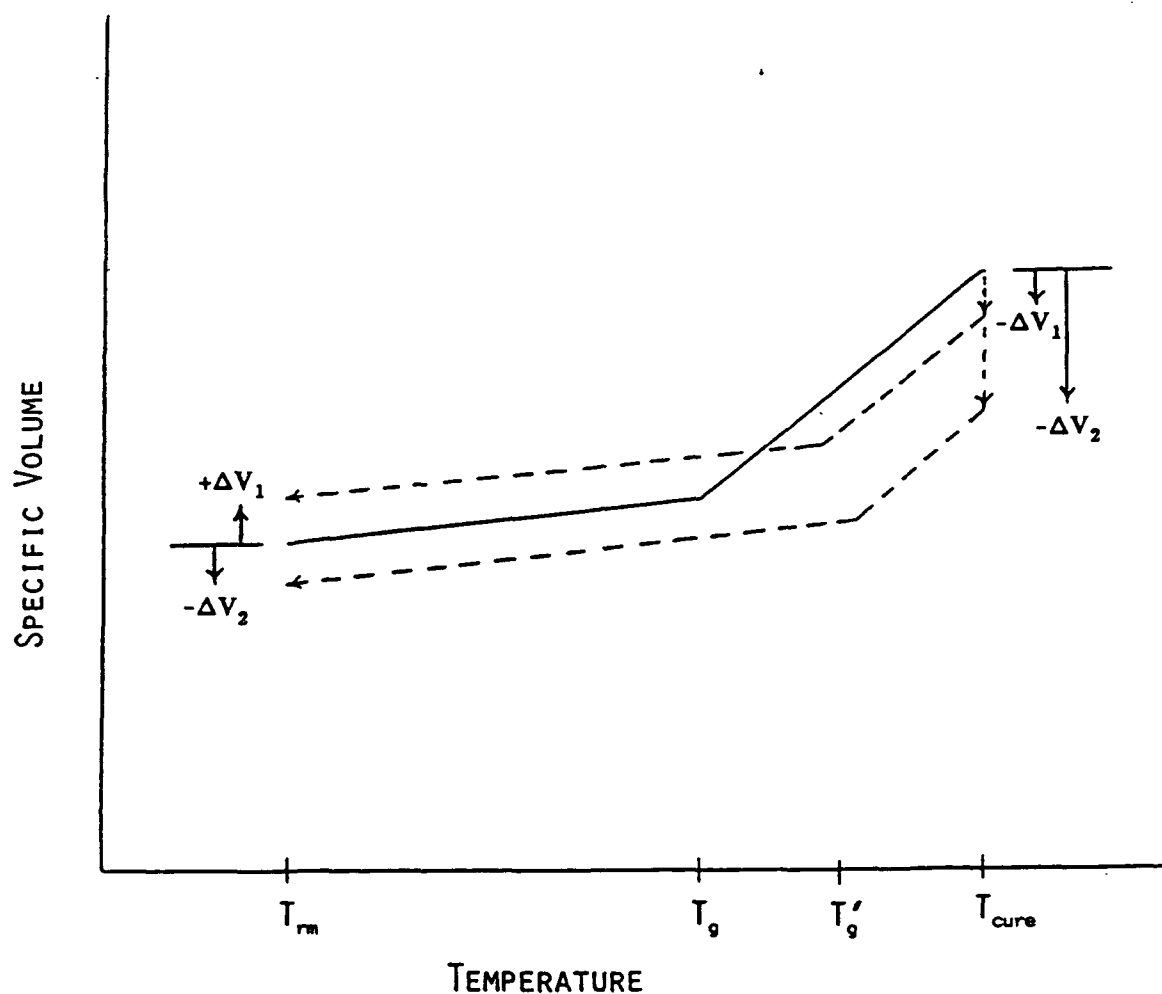


Fig. 7. Glass transition temperature dependence on cyanate conversion for bisphenol A dicyanate resin.



CASE 1: SMALL CURE SHRINKAGE

CASE 2: LARGE CURE SHRINKAGE

Fig. 8. Sketch indicating how cure advancement with consequent glass transition temperature increase ( $T_g$  to  $T'_g$ ) may cause specific volume change in opposite directions (case 1) depending on the temperature of measurement (room temperature vs. cure temperature).

### Propagation of Errors.

The propagation of errors equation is obtained by taking the total differential of Equation 1 considering  $W_p$ ,  $h$ ,  $W_{Hg}$  and  $T$  to be variables.

$$\begin{aligned} dv_{sp} = & \{ (1/W_p) c (1 + \beta_{py} (T - 25)) \} dh - \{ (1/W_p) V_{sp, Hg} (1 + \beta_{Hg} T) \} dW_{Hg} - \\ & \{ (1/W_p^2) [(ch + V_B) (1 + \beta_{py} (T - 25)) + c(\Delta h) (\beta_{Hg} - \beta_{py}) (\Delta T) - \\ & W_{Hg} (V_{sp, Hg} (1 + \beta_{Hg} T))] \} dW_p + \{ (1/W_p) [(ch + V_B) \beta_{py} - \\ & W_{Hg} V_{sp, Hg} \beta_{Hg}] \} dT \end{aligned} \quad (4)$$

Equation 4 has the utility of assigning error contributions to each of these source variables. By assigning reasonable experimental numbers to the variables and conservative estimates for the accuracy in the differential terms as presented below, the magnitude of these error contributions can be calculated.

$W_p \approx 1.0 \text{ g}$	$dh \approx 0.05 \text{ cm}$
$c \approx 0.0087 \text{ ml/cm}$	$dW_p \approx 0.0005 \text{ g}$
$T \approx 200^\circ\text{C}$	$dW_{Hg} \approx 0.001 \text{ g}$
$h \approx 20 \text{ cm}$	$dT \approx 2^\circ\text{C}$
$W_{Hg} \approx 25 \text{ g}$	
$V_B \approx 2.5 \text{ ml}$	

Inserting these values into Equation 4 yields the following calculated result. The corresponding source variable derivative terms from Equation 4 are listed in the parenthesis below. No single variable dominates the error in the measurement.

$$dv_{sp} = 0.00043 \quad - \quad 0.00008 \quad - \quad 0.00039 \quad - \quad 0.00062$$

(dh)                      (dW<sub>Hg</sub>)                      (dW<sub>p</sub>)                      (dT)

### Repetitive Measurements.

A series of 8 repetitive measurements were made on a partially cured bisphenol A dicyanate resin plug by 2 operators employing the same dilatometer apparatus and procedure. The dilatometer was dismantled and cleaned between each measurement. The eight specific volume measurements, arithmetic mean and

standard deviation are presented below.

$V_{sp}(\text{ml/g})$

0.8072  
0.8085  
0.8106  
0.8110  
0.8094  
0.8081  
0.8103  
0.8077

$$\bar{V}_{sp} = 0.8091 \text{ ml/g}$$

$$\sigma_n = 0.0013 \text{ ml/g}$$

The standard deviation is more than twice as large than would be anticipated from the propagation of errors. Two other sources of error may be considered; vacuum quality during mercury filling and joint grease seepage.

Considering vacuum quality, with the mechanical pump currently in use, it can range from 0.005 mm as a good vacuum to 0.025 mm as a poor vacuum. It is possible to calculate what the corresponding differential quantity of air might contribute to the measurement using approximate values of 3 ml for the dilatometer volume and 800 mm (1 atm + 40 cm mercury in capillary) for the dilatometer pressure.

$$\text{poor vacuum} \quad V_{air} = (0.025/800)3.0 = 0.00009 \text{ ml}$$

$$\text{good vacuum} \quad V_{air} = (0.005/800)3.0 = 0.00002 \text{ ml}$$

Thus, the vacuum quality is too small to be a factor in the measurement variation.

The vacuum grease on the bulb joint may be the factor. The extremes in the measurement are separated by 0.0038 ml. With a density close to 1, this represents 3.8 mg of grease. Any grease squeezed inside the effective dilatometer volume will have the effect of contributing to the polymer volume but not to the mass. The error then becomes proportional to the volume ratio of grease seepage to resin. As discussed in Section II, the grease application is a manual process subject to variation.

#### ACKNOWLEDGEMENT

Authors express appreciation to Jed Macosko for some of the dilatometer measurements and acknowledge Office of Naval Research as sponsor for this investigation.

## REFERENCES

1. W. Ostwald, Manual of Physio-Chemical Measurements, MacMillan and Co., New York, 1894.
2. N. Bekkedahl, J. Res. Natl. Bur. Stand., 43, 145 (1949).
3. P.S. Wilson and R. Simha, Macromolecules 6, 902 (1973).
4. L.C. Rubens and R.E. Skochdopole, in Encyclopedia of Polymer Science and Technology, Vol. 5, John Wiley & Sons, Inc., New York, 1966, p. 83.
5. P. Zoller, in Encyclopedia of Polymer Science and Engineering, Vol. 5, Wiley-Interscience, New York, 1986, p. 69.
6. L.C. Rubens and R.E. Skochdopole, J. Appl. Poly. Sci., 9, 1487 (1965).
7. B. Yates, B.A. McCalla, L.N. Phillips, D.M. Kingston-Lee, and K.F. Rogers, J. Mater. Sci., 14, 1207 (1979).
8. I-C. Choy and D.J. Plazek, J. Poly. Sci. Poly. Phys. Ed., 24, 1303 (1986).
9. H. Pingsheng, Z. Zhiqiang and P. Caiyuan, J. Mater. Sci., 24, 1528 (1989).
10. O.S. Tyagi and D.D. Deshpande, J. Appl. Poly. Sci., 37, 2041 (1989).
11. Calculated from reference 2 values of mercury specific volume at 0°C and temperature coefficient of specific volume (i.e.  $0.0000134 \text{ ml/g}^\circ\text{C} \div 0.073554 \text{ ml/g}$ ).